

# LAI-OPEN PATENT GAZETTE

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Title of the invention: Method of heat-treating an iron or steel material

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## Claims:

(1) A method of heat-treating an iron or steel material, comprising the steps of

covering the surface of an iron or steel material with a slurry-like covering material adjusted in pH to 5 or less prepared by adding 20 to 65% of (based on the weight of the dispersion medium composed of a silica sol or an alumina sol described later) a dispersion medium consisting of one more of clay minerals of kaolin group and bauxite group, and  $Al_2O_3$ , to a dispersion medium composed of a silica sol containing fine silicic acid particles of 100 m $\mu$  and smaller in particle size

or an alumina sol containing fine alumina particles of 100 mμ and smaller in particle size, and adding further a dispersion medium composed of 25% or less of aluminum biphosphate, or 20% or less of ethyl silicate, or 5 to 40% or less of both the compounds in total, to keep the amount of silicic acid particles at 5 to 40% or to keep the amount of Al<sub>2</sub>O<sub>3</sub> particles at 3 to 30% in the entire mixture, and

heating.

(2) A method of heat-treating an iron or steel material, comprising the steps of

covering the surface of an iron or steel material with a slurry-like covering material adjusted in pH to 5 prepared by adding 20 to 65% of (based on the weight of the dispersion medium composed of a silica sol or an alumina sol described later) a dispersion medium consisting of one more of clay minerals of kaolin group and bauxite group, and Al<sub>2</sub>O<sub>3</sub>, to a dispersion medium composed of a silica sol containing fine silicic acid particles of 100 mμ and smaller in particle size or an alumina sol containing fine alumina particles of 100 mμ and smaller in particle size, and adding further 25% or less of aluminum biphosphate, or 20% or less of ethyl silicate, or 40% or less of both the compounds in total, to keep the amount of silicic acid particles at 5 to 40% or to keep the amount of Al<sub>2</sub>O<sub>3</sub> particles at 3 to 30% in the entire mixture, further adding 5 to 40% (based on the weight of the dispersion

medium composed of the silica sol or alumina sol) of feldspar  
and/or talc, and  
heating.

### Detailed description of the invention:

The present invention relates to a method of heat-treating an iron or steel material for preventing oxidation, surface flaws and form defects, <sup>and</sup> in more detail, a method of heat-treating an iron or steel material, for preventing oxidation, sulfidization and the surface flaws and scale production caused by surface enrichment of non-oxidizing elements, etc., in the case where a steel piece such as a slab, billet or bloom or a shaped steel piece such as a beam or a crank is heat-treated in a heating furnace or soaking pit, or for preventing the scale production caused with oxidization, sulfidization, etc. in the case where an iron or steel product such as a steel plate, shape steel or bar steel is heated in a heating furnace or heat treatment furnace.

In general when an iron or steel material is heated at high temperature in an oxidizing atmosphere in a soaking pit or heating furnace, scale production and surface flaws occur.

Especially in cases of ordinary carbon steels, and ~~also~~ chromium-containing steels, manganese-containing steels, silicon-containing steels, nickel-containing steels, and so on, the scale production and surface flaws are liable to occur.

If any of these steels is heated at high temperature in an oxidizing atmosphere, the contained elements are remarkably oxidized and sulfidized, and enrich the surface, to produce scale, and when the surface is descaled, they cannot be easily removed while surface flaws are also liable to occur. Furthermore, if a steel billet having blowholes, skin holes, inclusions, etc. formed

immediately below the surface during ingot making is heated at high temperature, they are exposed as surface flaws with the progression of oxidation.

For preventing the above-mentioned oxidation caused when such a steel material is heated at high temperature in an oxidizing atmosphere, it is practiced to cover the surface of the steel material to be heated, for preventing that the oxidizing atmosphere comes into contact with ~~contacts~~ the surface of the steel material to be heated.

As such publicly known oxidation-preventing covering materials, known are liquids obtained by adding water or an organic solvent, etc. to a mixture consisting of an oxide such as alumina, silicon oxide, chromium oxide or clay mineral, an element or alloy of aluminum, carbon, silicon, ferroaluminum, ferrosilicon, etc., a clay mineral such as water glass or bentonite, and a caking agent such as sugar, amine or ester. Any of these covering materials is applied to a steel material before heating by means of spraying, brushing or roll coating, etc., and the covered steel material is dried and heat-treated in a heating furnace, etc.

However, these publicly known covering materials cannot sufficiently achieve the purpose in industrial practical application and have various problems.

The present invention has been achieved as a result of various studies made for the purpose of <sup>developing</sup> ~~development~~ a covering material free from the above-mentioned defects.

The present invention is characterized in that groups (A), (B) and (D) are selected from the following groups, that one or

more materials are selected in each group, that a mixture consisting of the selected materials and, as required, the material of group (C) is applied to the surface of the iron or steel material to be heated, and that the iron or steel material is heat-treated.

Group A: A silica sol or alumina sol of pH 5 or lower containing fine particles of silicic acid or alumina of 100 mμ and smaller in particle size dispersed in water and/or organic solvent

Group B: A clay mineral of kaolin group (kaolin, halloysite, metahalloysite) or bauxite group (boehmite, gibbsite), or metal oxide such as  $Al_2O_3$

Group C: Feldspar or talc

Group D: Aluminum biphosphate or ethyl silicate

In this invention, an iron or steel material to be heated is covered on the surface with the above-mentioned covering material by means of coating, etc., before heat treatment. The covering material used in this invention is excellent in the property of covering iron and steel materials, very small in scale production after heat treatment, and very excellent in the releasability by means of air cooling or water cooling, etc.

The covering material used in the method of this invention is described below in detail.

The silica sol or alumina sol of said group (A) as a dispersion medium of the covering material of this invention is a sol solution containing fine particles of silicic acid or alumina of 100 mμ and smaller in particle size dispersed in water and/or organic solvent such as methanol and adjusted to pH 5 or less.

The silicic acid particles or alumina particles constituting said dispersion medium in this invention must be fine particles, to have electric charges on their surfaces for having a bonding nature, and they should be 100  $\mu$  and smaller in particle size respectively. Such inorganic very fine particles having excellent bondability and electric charges can act to fill and cover the defective portions (pinholes) as a covering layer and act to be bound to the steel material for forming a stable covering layer. Therefore, in this invention, if the respective particles are smaller, better results can be obtained. If the particle size is larger than 100  $\mu$ , the above-mentioned binding action cannot be obtained, and the object of this invention cannot be achieved.

In this invention, a dispersion medium consisting of one or more of clay minerals of bauxite group and kaolin group and alumina is added to the dispersion medium composed of said sol solution, and the additive prevents the oxidation of the steel material otherwise caused by heating at high temperature in an oxidizing and atmosphere,  $\Delta$  is excellent in fire resistance,  $\Delta$  and has covering power and is little changed in volume by heating. The additive having particles under a 100-mesh sieve is suitable for obtaining coatability and uniformity. Furthermore, the amount of the dispersion medium consisting of one or more of clay minerals of bauxite group and kaolin group and alumina should be 20 to 65 wt% based on the weight of the dispersion medium composed of said sol solution. If the amount is less than 20%, the covering material sags during covering work, making it difficult to achieve uniform

covering. On the other hand, if the amount is more than 65%, it becomes difficult to homogeneously mix the dispersion medium in the sol solution, and furthermore, high viscosity makes uniform covering difficult.

Moreover, 25% or less of aluminum biphosphate or 20% or less of ethyl silicate is added to modify the covering material, i.e., to lower the pH of the covering material. In addition, the aluminum biphosphate having a three-dimensional network structure with heating improves the heat resistance of the covering material and promotes the effect of preventing oxidation. On the other hand, ethyl silicate improves the bonding strength to the iron or steel material after coating and drying and improves rust prevention.

If the amount of aluminum biphosphate is more than 25% based on the weight of said alumina sol or silica sol, drying after covering takes a long time to inconvenience working, though the intended effects can be obtained correspondingly. If the amount of ethyl silicate is more than 20%, the viscosity of the covering material rises to impair the storage stability and uniform coatability. So, their amounts should not exceed the respective upper limits. When aluminum biphosphate and ethyl silicate are added as a mixture, the total amount of them should be 40% or less. If the amount is more than 40%, the amount of alumina or silica decreases relatively, and the object of this invention cannot be achieved.

In the case where aluminum biphosphate and/or ethyl silicate is added, the content of silicic acid particles in said sol solution

can be decreased to a lower limit of 5%, and the content of alumina particles can be decreased to a lower limit of 3%.

Said silicic acid or alumina is a material having a network structure with excellent heat resistance, and since it is homogeneously dispersed in the covering material of this invention, the effect of intercepting the atmosphere during heating is large.

Said sol solution should contain 5 to 40% of silicic acid particles or 3 to 30% of alumina particles, and if the respective contents are smaller than the respective lower limits, the intended effects of this invention cannot be obtained.

On the other hand, if the respective contents are larger than the respective upper limits, the viscosity of the covering material of this invention becomes high, making it difficult to uniformly cover the iron or steel material. Furthermore, it becomes difficult to store or handle the covering material.

The pH of the sol solution is adjusted to 5 or less. If the sol solution is made acidic, during drying or heating after covering with the covering material in this invention, the iron oxide on the surface of the steel material is dissolved, and the dissolved material and the covering material are bound to each other, to promote the production of a thin gas impermeable layer on the under surface of the covering layer (the surface of the covering layer in contact with the steel material after heating). So, in this invention, the pH of the sol solution should be kept at 5 or less, and if the pH is more than 5, the above-mentioned action cannot be obtained.

The covering material used in the first subject matter of this invention has been described. The covering material in the second subject matter of this invention further contains feldspar and/or talc in addition to the above-mentioned covering material. In the case where particles of alumina, kaolin, etc. in the covering material are sintered, feldspar and talc act to compact those particles and to prevent the change of them in volume, and 5 to 40% of feldspar and/or talc should be added as fine particles under a 100-mesh sieve. If the amount is less than 5%, the intended effects cannot be obtained. On the other hand, if it is more than 40%, fire resistance declines in the case of feldspar, or the effect of decreasing the thermal expansion coefficient cannot be obtained <sup>thus being uneconomical.</sup> ~~uneconomically~~ in the case of talc, <sup>^</sup> The inventors found that when the amount of feldspar or talc is 10 to 30%, the most preferable results could be obtained.

As described above, the covering material of this invention consists of groups A + B + D or A + B + C + D selected from respective groups (A), (B), (C) and (D). As described above, the covering material has a composite synergism, and can be a very excellent oxidation preventive covering material for heat treatment of an iron or steel material at high temperature.

Said covering material can be applied to the surface of an iron or steel material to be heated, by a publicly known covering means such as brushing, spraying or roller coating. It is recommended that the covering thickness should be in a range of 30 to 1000  $\mu$ , especially 50 to 500  $\mu$ . If the covering thickness

is too thin, the effect of intercepting the atmosphere during heat treatment cannot be sufficiently obtained.

An iron or steel material uniformly covered on the surface with said covering material is heat-treated in a treating furnace such as a heating furnace.

After completion of heat treatment, the covering layer can be easily released by means of air cooling or water cooling (including descaling with high pressure water), etc.

The covering material of this invention is very good in releasability after completion of heat treatment, and since uniform cooling can be made after removal of the covering material, uniform hardenability can be greatly improved, <sup>thus being advantageous.</sup> ~~advantageously~~

Therefore, the form defects such as edge waviness and center waviness of the iron or steel material after cooling can be prevented.

The heat treatment method of this invention is as described above. The covering material used in this invention can generally contain powders of metals prone liable to be oxidized such as aluminum, magnesium and chromium, and  $\text{Cr}_2\text{O}_3$  used in heat-resistant covering materials, etc., to such an extent that the object of this invention is not impaired.

#### Example 1

A 10 mm thick steel sheet of 100 x 100 mm was ground on the surface with shot blasting, covered with any of the covering materials composed as listed in Table 1, dried, heat-treated in atmosphere, and immediately cooled for releasing the covering

material and descaling. The results of this experiment and the results of heat treatment made without using any covering material are shown in Table 2.

Table 1 Compositions of covering materials

No.	Composition	pH
1	34.5% kaolin - 11.5% feldspar - 2.7% silica sol aqueous solution - 21.5% silica sol methanol aqueous solution (21.5: SiO <sub>2</sub> ) - 5.5% ethyl silicate (containing 11.8% of SiO <sub>2</sub> particles of 100 $\mu$ and smaller)	3.6
2	36% kaolin - 12% talc - 12% aluminum primary phosphate - 40% methanol silica sol (containing 12% of SiO <sub>2</sub> particles of 100 $\mu$ and smaller)	1.9
3	30% kaolin - 10% feldspar - 60% silica sol aqueous solution (comparative material) (containing 12% of SiO <sub>2</sub> particles of 100 $\mu$ and smaller)	7.5
4	33% kaolin - 11% feldspar - 56% silica sol aqueous solution (comparative material) (containing 11.2% of SiO <sub>2</sub> particles of 100 $\mu$ and smaller)	7.1

Table 2

Steel	Covering material	Covering conditions and covering states				Heat treatment and covering releasing conditions		Results of heat treatment test	
		Covering method	Drying conditions	Covering thickness	Adhesive strength	Heat treat conditions	Release method	Releasability Appearance	Oxidation prevent rate
A	1	Spray coating	80°C 3 min	150 $\mu$	◎	950°C 60 min	5 kg/cm <sup>2</sup> water pressure spray	◎ (very good)	1/8
	2	Brushing	80°C 3 min	300 $\mu$	◎	950°C 60 min	5 kg/cm <sup>2</sup> water pressure spray	◎ (very good)	1/7
	Nil	-	-	-	-	950°C 60 min	5 kg/cm <sup>2</sup> water pressure spray	X (poor descaling)	1
B	3	Immersion - roll squeezing	150°C 20 min	500 $\mu$	△	1250°C 3 hours	5 kg/cm <sup>2</sup> water pressure spray	△ (partially remain)	1/2
	Nil	-	-	-	-	1250°C 3 hours	5 kg/cm <sup>2</sup> water pressure spray	X (poor descaling)	1

Notes:

Adhesive strength of covering material in the table

◎: Very good ○: Good △: Rather poor

Releasability and appearance of covering material in the table

◎: Very good ○: Good △: Rather poor X: Very poor

The oxidation prevention rate in the table was calculated from the following formula:

Oxidation prevention rate =  $[1 - (\text{Weight of steel material after heat treatment of covered steel material}) / (\text{Weight of steel material before heat treatment of covered steel material})] / [1 - (\text{Weight of steel material after heat treatment of non-covered steel material}) / (\text{Weight of steel material before heat treatment of non-covered steel material})]$

Example 2

A hot rolled steel sheet for low temperature having about 30 to 40  $\mu$  of hot rolling scale deposited was covered with a slurry-like covering material of pH 1.9 obtained by mixing 36% of kaolin, 12% of potash feldspar, 10% of aluminum primary phosphate aqueous solution and 42% of silica sol aqueous solution (containing 8.4% of  $\text{SiO}_2$  particles of 100  $\text{m}\mu$  and smaller)<sup>up</sup> to a thickness of 75  $\mu$  by means of spraying, dried naturally at room temperature for 5 hours, and heat-treated in a 950°C heating furnace for 60 minutes, <sub>and</sub> had the covering material removed using a descaling device with a water pressure of 75  $\text{kg}/\text{cm}^2$ , and was immediately hardened with water.

As a result, from the steel sheet covered with the covering

material, the covering material could be entirely and uniformly removed by means of descaling, and the mill scale deposited before heat treatment could also be uniformly removed. The appearance was smooth and good. Also the form of the steel sheet was very good with little edge waviness, center waviness, etc., and the fluctuation of hardness was very small, to show that uniform hardening could be accomplished.

On the other hand, a steel sheet not covered with the covering material was heat-treated in the same way. The removal of mill scale and the scale produced below the mill scale by air cooling and descaling was poor and non-uniform, and edge waviness, center waviness, etc. occurred remarkably to degrade the appearance of the form. Furthermore, hardening was very irregular. The oxidation prevention rate of the steel sheet treated according to the present invention was about 1/5.

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